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AVIATION TURBINE FUEL LUBRICITY EVALUATION OF CORROSION INHIBITORS

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FUELS BRANCH
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This report presents the results of the Air Force fuel lubricity program which dealt with the evaluation of corrosion inhibitors as lubricity agents in jet aircraft fuels. This study was conducted by Joseph Petrarca, Jr., of the Fuels Branch, Fuels and Lubrication Division, and is documented under work unit 30480543.

This report has been reviewed by the Information Office (ASD/OIP) and is releasable to the National Technical Information Service (NTIS). At NTIS, it will be available to the general public, including foreign nations.

This technical report has been reviewed and is approved for publication.

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20. ABSTRACT (Continue on reverse side if necessary and identify by block number)

This report describes the evaluation of the effectiveness of corrosion inhibitors as fuel lubricity agents. The study was conducted with the Furey Ball-on-Cylinder. In the study, the eleven corrosion inhibitors from QPL-25017-9 were evaluated as lubricity agents in three base fluids, at various concentrations, and at the two base fluid temperatures of 75°F and 150°F. The rank effectiveness of the inhibitors correlated for the following two cases:

1. The inhibitors at their maximum allowable concentration in the three base fluids at 75°F.

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20 Abstract Continued

2. The inhibitors at three concentrations in the same base fluid at 75°F.

The rank effectiveness of the inhibitors did not correlate for the case where the corrosion inhibitors were at their maximum allowable concentrations in the same base fluid but at the two different temperatures of 75°F and 150°F.

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INTRODUCTION

In 1965, the U.S. Air Force experienced major aircraft field lubricity problems. The lubricity problem involved aircraft which contained the J57, J69, and J79 engines. When the pilot tried to decelerate the aircraft, the corresponding response from the fuel control was either sluggish or nonexistent. When a hung-up fuel control was examined, a spool/sleeve servo system was found to be malfunctioning. The malfunction was caused by the poor lubricity JP-4 fuel which did not contain corrosion inhibitors. The servo valve was not receiving adequate lubrication from the fuel.[1] The fuel lubricity problem was corrected by the requirement that JP-4 fuel contain a corrosion inhibitor.

In U.S. commercial aircraft, suspected lubricity problems have occurred in the JT-9 and JT8 engine fuel pumps. These pumps experience excessive gear tooth and spline wear. The two wear problems are believed to be caused by separate mechanisms, which are scoring wear and fretting corrosion, respectively. The number of JT-9 pump failures has been reduced by the use of HITEC E-515, a corrosion inhibitor, in wide cut fuels and through improved pump design.[2] In the United Kingdom, the lubricity problem has been much more severe and reoccurrent. It has affected both the military and commercial aircraft. In 1972, there were three pump failures on commercial aircraft.

In the first quarter of 1973, the pump failures on commercial aircraft rose to 11. However, the RAF has been free of lubricity problems since they began using HITEC E-515 (a corrosion inhibitor) in their service fuel. Its usage began in late 1971 or early 1972.

Since 1965, the Air Force has strived to establish a test device which will measure the lubricity of a fuel. Four mechanical lubricity devices, which are only a fraction of the number available, were examined by the Air Force from 1965 to present. They are the Four Ball Tester, the Vickers Vane Pump, the Furey Ball-on-Cylinder, and the Bendix CRC Lubricity Simulator.

The objective of the Air Force program was to determine the effectiveness of lubricity additives using a mechanical test device. In this report, the lubricity additives studied were corrosion inhibitors from QPL-25017-9. The effectiveness of each additive was examined for the three parameters below:

(1) Different base fluids

(2) Various additive concentrations

(3) Elevated Temperatures

The device used for the evaluation was the Furey Ball-on-Cylinder.

SECTION II

BALL-ON-CYLINDER BASE FLUID STUDY

As stated in the introduction, the objective of this program was to determine the effectiveness of fuel lubricity additives with the Ball-on-Cylinder device. The Furey Ball-on-Cylinder device is a mechanical tester. In consists of a stationary ball which is perpendicularly loaded and is in contact with a cylinder. The cylinders and balls are made from AISI 52100 steel with a hardness of 21.5 and 63 Rockwell C, respectively. The cylinder and ball are located in a rectangular test cell. The cylinder is approximately one-third immersed in the test fluid. The remaining portion of the cylinder and the ball are exposed to a controlled environment consisting of water pumped air having a moisture content of less than 20 ppm. The standard operating conditions for the Ball-on-Cylinder tests are: 1000 gm load, 240 rpm cylinder speed, dry air environment with .5 ft^3/min indirect purging, and 75°F fuel temperature.

The test sequence for the Ball-on-Cylinder is as follows: (1) mount the cylinder in the test cell; (2) clean the ball, cylinder, and test cell; (3) place the ball in the chuck and install the assembly on the rig; (4) add 50 ml of fluid to the test cell; (5) begin rotating cylinder at 240 rpm; (6) purge test cell with compressed dry air for 15 minutes; (7) place the loaded ball in contact with the rotating cylinder for 32 minutes while maintaining the air flow into the test cell; (8) terminate the test; and (9) measure the major and minor axes of the elliptical wear pattern on the

ball and record the average value as the wear scar diameter, WSD. In step 2, the materials are cleaned by rinsing them with three reagent grade solvents in the following order; acetone, propanol, and petroleum ether.

For the test program, a suitable base fluid was needed. In general, the base fluid must be sufficiently poor in lubricity in order that the relative effectiveness of the additives can be distinquished at low concentrations. Also, the relative effectiveness of the inhibitors in the base fluid should be similar to the relative effectiveness of the same additives in JP-4.

In the specific case of the Ball-on-Cylinder tester, a secondary requirement for the base fluid existed due to restrictions created by the test device. It was found that the purging of the test cell with dry air tended to excessively evaporate a fluid such as isooctane. Therefore, a base fluid must have a low volatility.

A question which often arises is, what criteria should be used to define a poor lubricity fuel? A poor lubricity fuel is a fuel which causes aircraft fuel system hardware to malfunction. Since fuel system hardware varies in different aircraft, a fuel may exhibit poor lubricity in some types of aircraft but not in all types. This was illustrated by the U.S. Air Force fuel lubricity problem in 1965. Ideally, a poor lubricity fuel can be identified by a mechanical lubricity test device if a limit is established for the device.

In 1966, a batch of the poor lubricity JP-4 fuel, which caused the U.S. Air Force aircraft lubricity problems, was tested on the Furey Ball-on-Cylinder by ESSO Research & Engineering Company under Contract

AF33(615)-2828. The fuel gave a wear scar diameter of .58 mm under a load of 1000 gms and a cylinder speed of 240 rpm. A second JP-4 fuel which did not cause lubricity problems gave a wear scar diameter of .38 mm.[3]

The only other data point for the Ball-on-Cylinder on a poor lubricity fuel was obtained on Teesport fuel. The Teesport fuel is a British AvTur which had caused the failure of an overhauled fuel pump in 1973 after only 142 hours of operation (normal life, 5000 hrs).[4] A 420,000 gallon batch of the fuel has been in storage at Derby, England since 1970. Through the assistance of the United Kingdom Ministry of Defense, 55 gallons of the fuel were shipped to Wright-Patterson Air Force Base in a steel drum in 1974. When the fuel was tested on the Ball-on-Cylinder under standard operating conditions, a wear scar diameter of .51 mm was obtained. However, any changes in the fuel which might have occurred during its four year storage or during its transfer to the U.S. would be expected to improve its lubricity. Thus, the wear scar diameter measured for the Teesport fuel is probably a lower limit for the lubricity condition of the fuel in 1973.

In 1973, the Air Force tested several JP-4 and Jet A-1 fuels on the Ball-on-Cylinder under standard operating conditions.[5] The maximum wear scar diameters measured were .47 and .49 mm respectively. Since no lubricity problems are known to have been encountered on these fuels, it appears a fuel which gives a wear scar diameter of .49 mm may have adequate lubricity. However, it takes hours of operation of a fuel control on a poor lubricity fuel to cause a malfunction and only

minutes of operation on good lubricity fuel to relieve the problem (Reference 1). Therefore, if a poor lubricity fuel is used in aircraft periodically, it may not cause any problems.

It is not possible to establish a lower limit on the wear scar diameter which corresponds to a poor lubricity fuel because of the limited data; however, it appears the limit is in the .50 mm to .58 mm range. Additional data from the Ball-on-Cylinder on known poor lubricity fuels is needed to refine the range.

In the course of this program three possible base fluids were investigated which had a suitable evaporation rate. They were a clay-treated JP-4, a clay treated JP-5, and Shell Sol 71. The wear scar diameters of the base fluids under standard operating conditions were .52 mm, .52 mm, and .73 mm, respectively and are within the range of a suspected poor lubricity fuel. The JP-4 and JP-5 had been clay-treated to remove the highly polar components and thereby worsen their lubricity. The Shell Sol 71 is a solvent comparable to Shell Sol T which is a calibration fluid used for the Lucas Dwell Meter. The typical properties at Shell Sol 71 and Shell Sol T are listed in Table I.

Eleven of the twelve corrosion inhibitors listed in QPL-25017-9 (Appendix B) were tested in each of the three base fluids with the Ball-on-Cylinder. The twelth additive, HITEC E-534, was not available. The test results with each inhibitor at its maximum allowable concentration according to QPL-24017-9 are given in Table II.

TABLE I

PROPERTIES OF SHELL SOL 71 and SHELL SOL T

Property	Shell Sol 71	Shell Sol T
Specific Gravity 60/60	.758	.760
Flash TCC °F	123	126
Distillation Range °F	346 - 399	367 - 417
Aromatics % V	.0	Below .5

TABLE II

EFFECTIVENESS OF LUBRICITY AGENTS AT MAXIMUM ALLOWABLE CONCENTRATION IN DIFFERENT BASE FLUIDS

	Wear Scar Diameter (mm)		
Additive	JP-4*	JP-5*	Shell Sol 71
None	.52	.52	.73
AFA-1	.53	.49	.73
LUBRIZOL 541	.42	.43	.52
TOLAD 244	.45	.48	.56
PRI-19	.39	.38	.44
HITEC E-515	.34	.36	.35
DCI-4A	.34	.33	.29
NALCO 5400-A	.50	.51	.59
UNICOR-J	.38	.36	.41
TOLAD 245	.37	.39	.43
CONOCO T-60	.31	.34	.36
NALCO 5402	.38	.41	.34

*Data from Reference 7

The correlations between the results in the different base fluids were examined by the use of the Spearman Rank Statistic (Appendix A). The calculated rank coefficients for the JP-4/JP-5 relationship and JP-4/Shell Sol 71 relationship were .907 and .873, respectively. This indicates both relationships correlate with a level of significance less than .1% i.e., there is less than one chance in a thousand that the correlations do not exist. Since both the JP-5 and the Shell Sol 71 results correlate with the JP-4 results at approximately equal levels of significance, either JP-5 or Shell Sol 71 is a suitable replacement base fluid for the JP-4 in this lubricity additive evaluation program.

The possible synergistic effects between the additives in the JP-4 base fluid and Shell Sol 71 or JP-5 were evaluated by applying the Wilcoxon Signed Rank Test (Appendix C) to the test results. For the JP-4/JP-5 relationship, the analysis indicated that there are no synergistic effects at a 5.4% level of significance; i.e., the additives appear to be equally effective in JP-4 and JP-5. For the JP-4/Shell Sol 71 relationship, the analysis indicated that there are synergistic effects at the 5.4% level of significanc . However, as previously stated, the relative effectiveness of the additives in JP-4 and Shell Sol 71 did correlate. Therefore, the synergistic effect is probably caused by the larger initial wear scar diameter (WSD) of 0.73 mm obtained with Shell Sol 71, as compared to the 0.52 mm WSD for JP-4. The larger base WSD results in a better separation of the wear scar diameters obtained with the different inhibitors. Therefore, the Shell Sol 71 was selected as the base fluid for the lubricity additive evaluation program.

SECTION III

EVALUATION OF LUBRICITY ADDITIVES AT VARIOUS CONCENTRATIONS

Corrosion inhibitors are required in JP-4 for lubricity reasons but are qualified by a corrosion test, MIL-I-25017C. One of the drawbacks of this test is that an additive will either pass or fail at a given concentration. The test does not tell to what degree the additive is effective at various concentrations.

There are three concentrations for corrosion inhibitors specified by MIL-I-25017C. The relative effective concentration is the concentration of the additive which just passes the corrosion test. The minimum effective concentration is the value of 1 1/2 times the relative effective concentration. It is also the minimum required in the fuel. Finally, the maximum allowable concentration for an additive is either 4 times its relative effective concentration or the concentration which just passes the WSIM test (the lower of the two).

The effectiveness of each inhibitor as a lubricity agent was investigated at various concentrations. The base fluid used was Shell Sol 71 for the reasons stated in Section II. The results for eleven inhibitors from QPL-25017-9 are shown in Figures 1 - 11. A smooth curve is drawn on each figure through the data points.

The concentration curves illustrate that the beneficial effects of the corrosion inhibitors can be detected at concentrations less than the relative effective concentration for each additive. The only exception is AFA-1 whose beneficial effects could not be detected at any concentration.

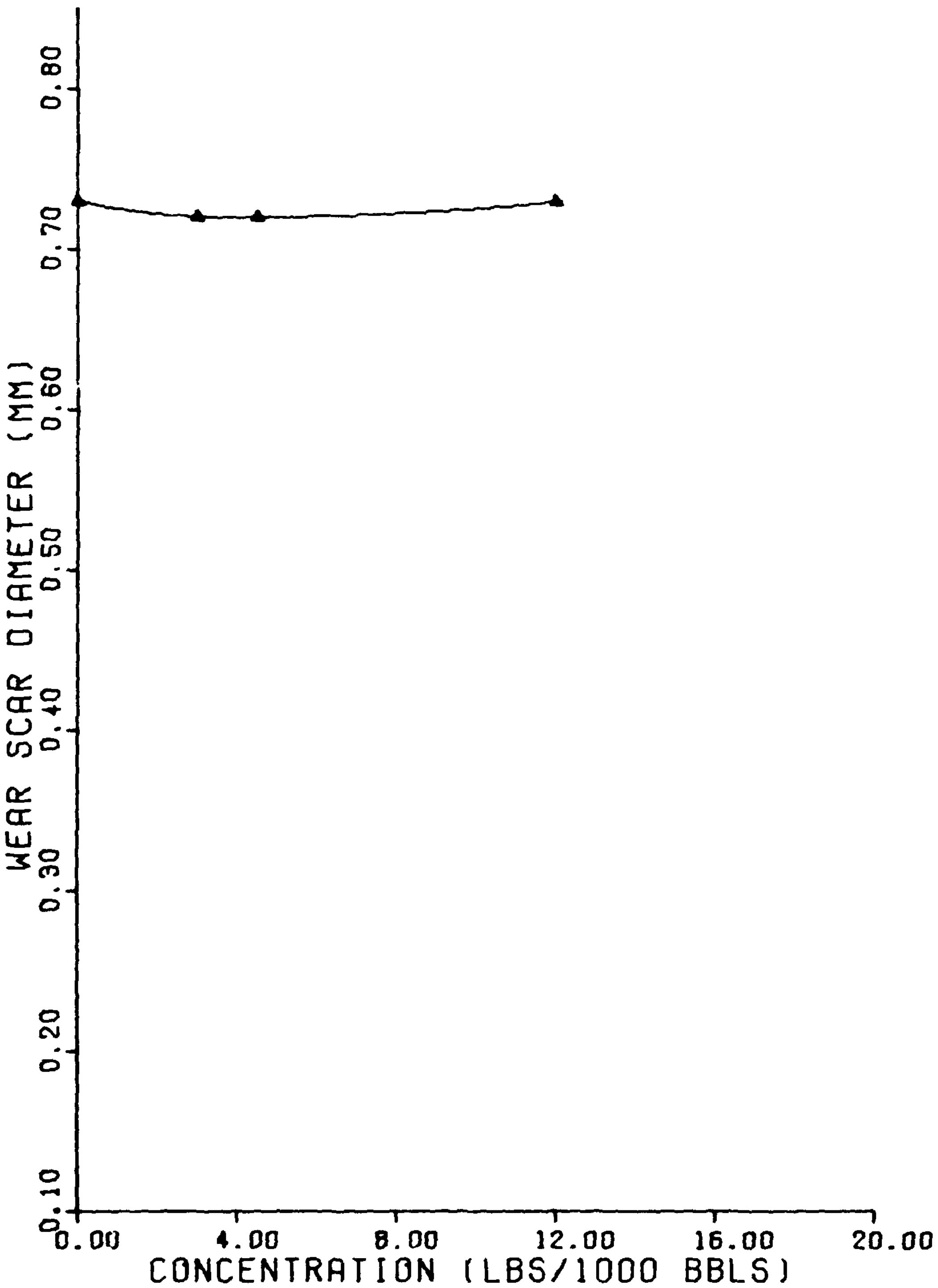

Figure 1. Wear Scar Diameter vs. Concentration of AFA-1 in Shell Sol 71

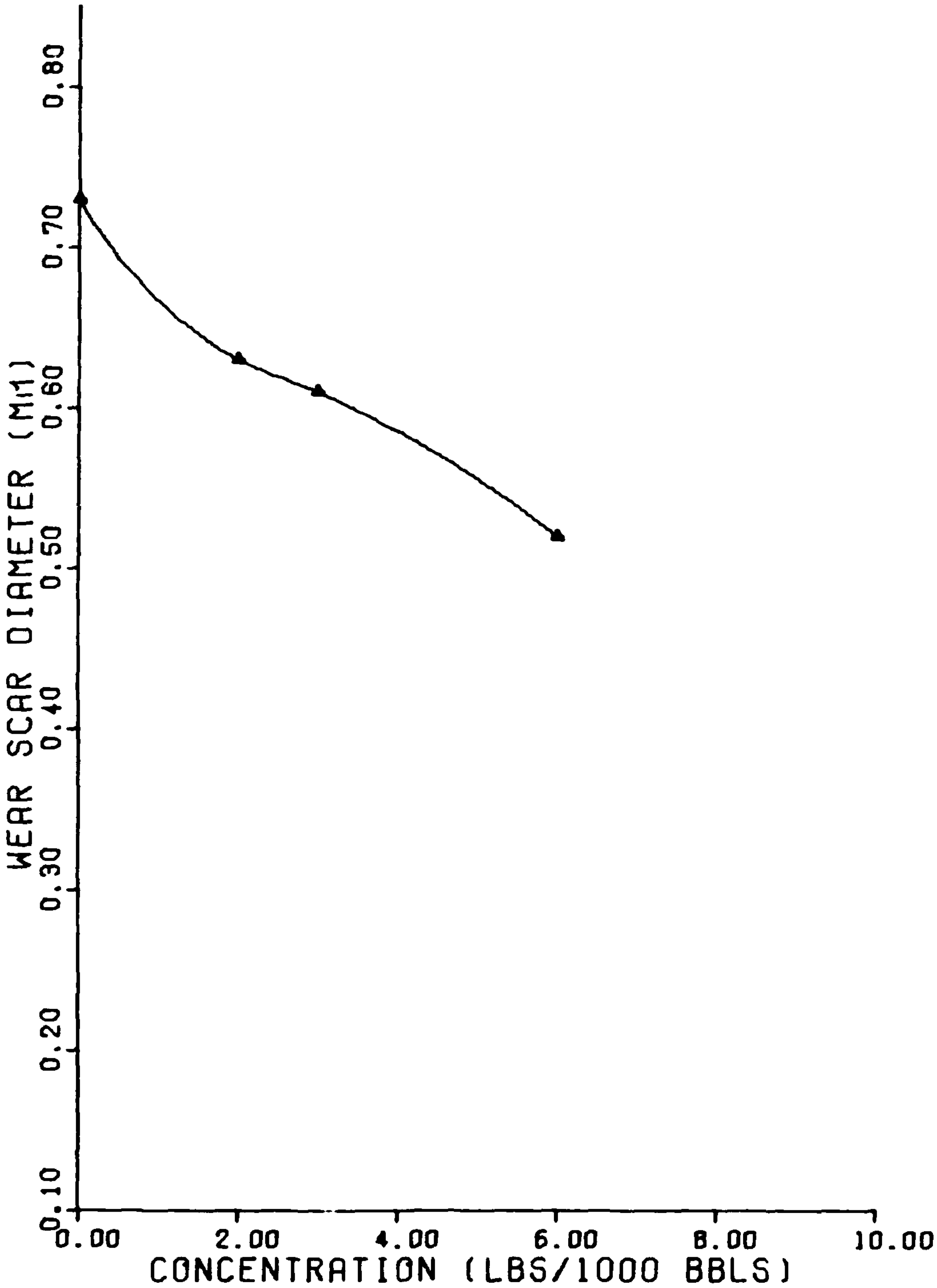

Figure 2. Wear Scar Diameter vs. Concentration of LUBRIZOL 541 in Shell Sol 71

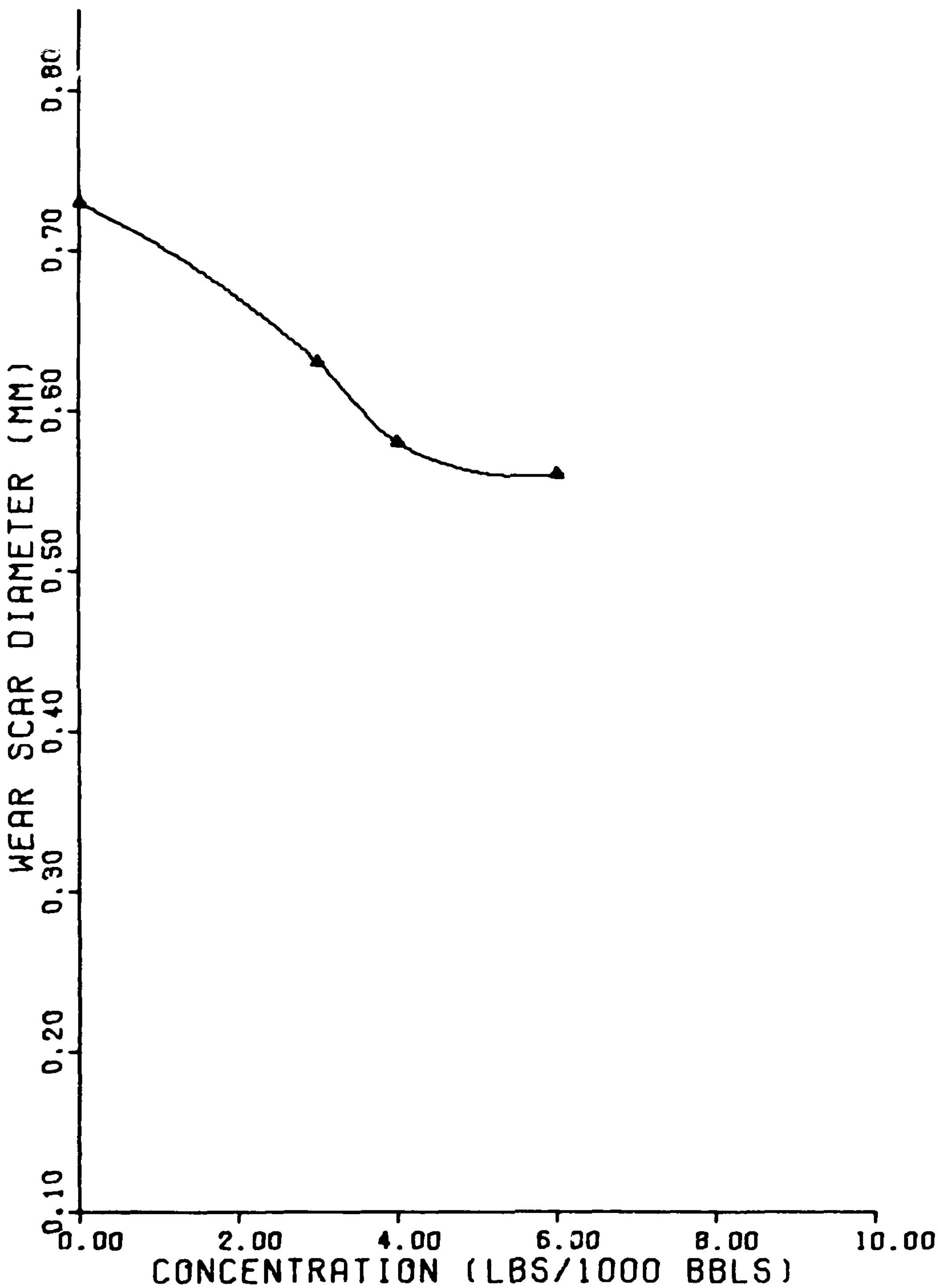

Figure 3. Wear Scar Diameter vs. Concentration of TOLAD 244 in Shell Sol 71

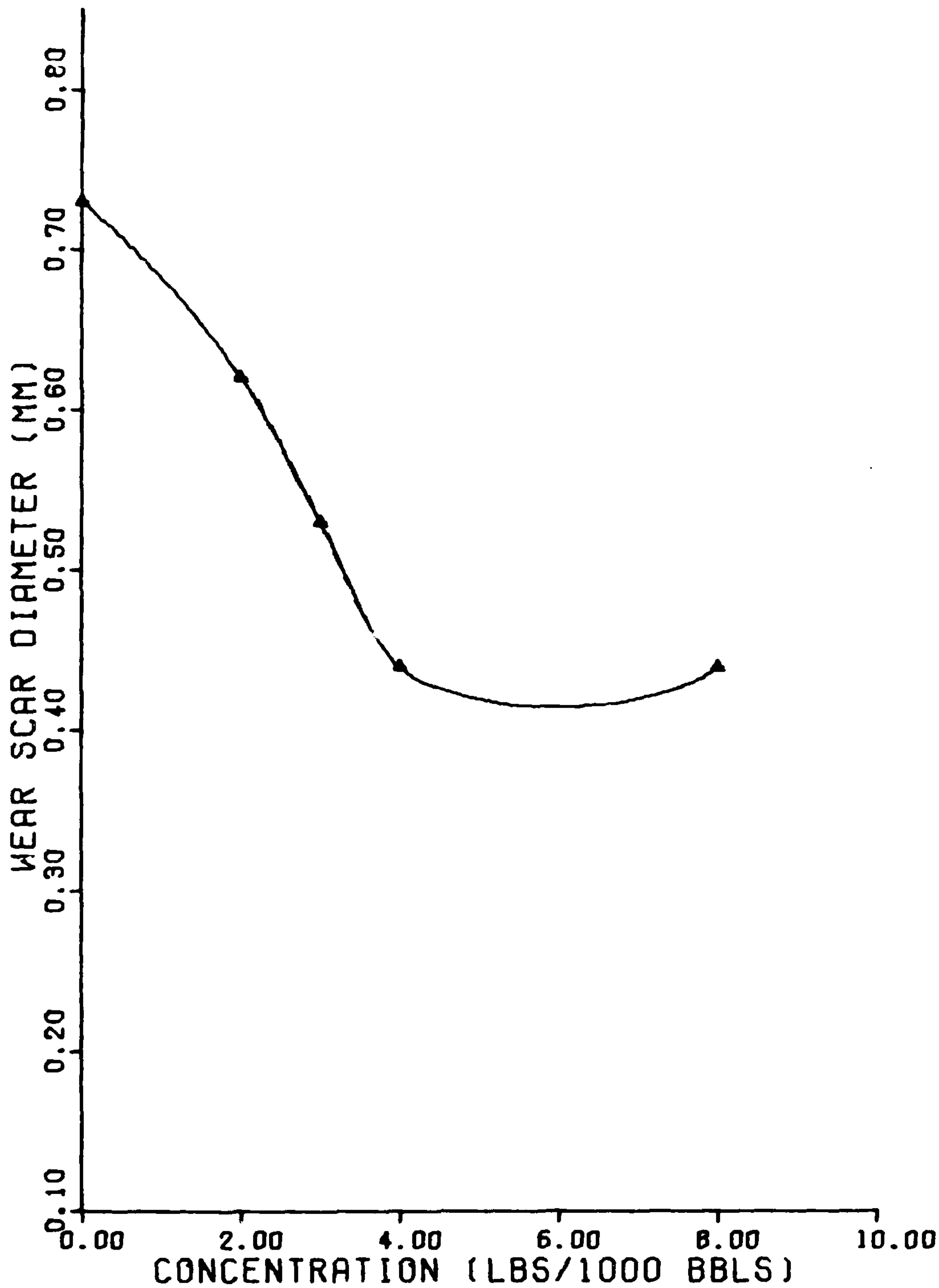

Figure 4. Wear Scar Diameter vs. Concentration of PRI-19 in Shell Sol 71

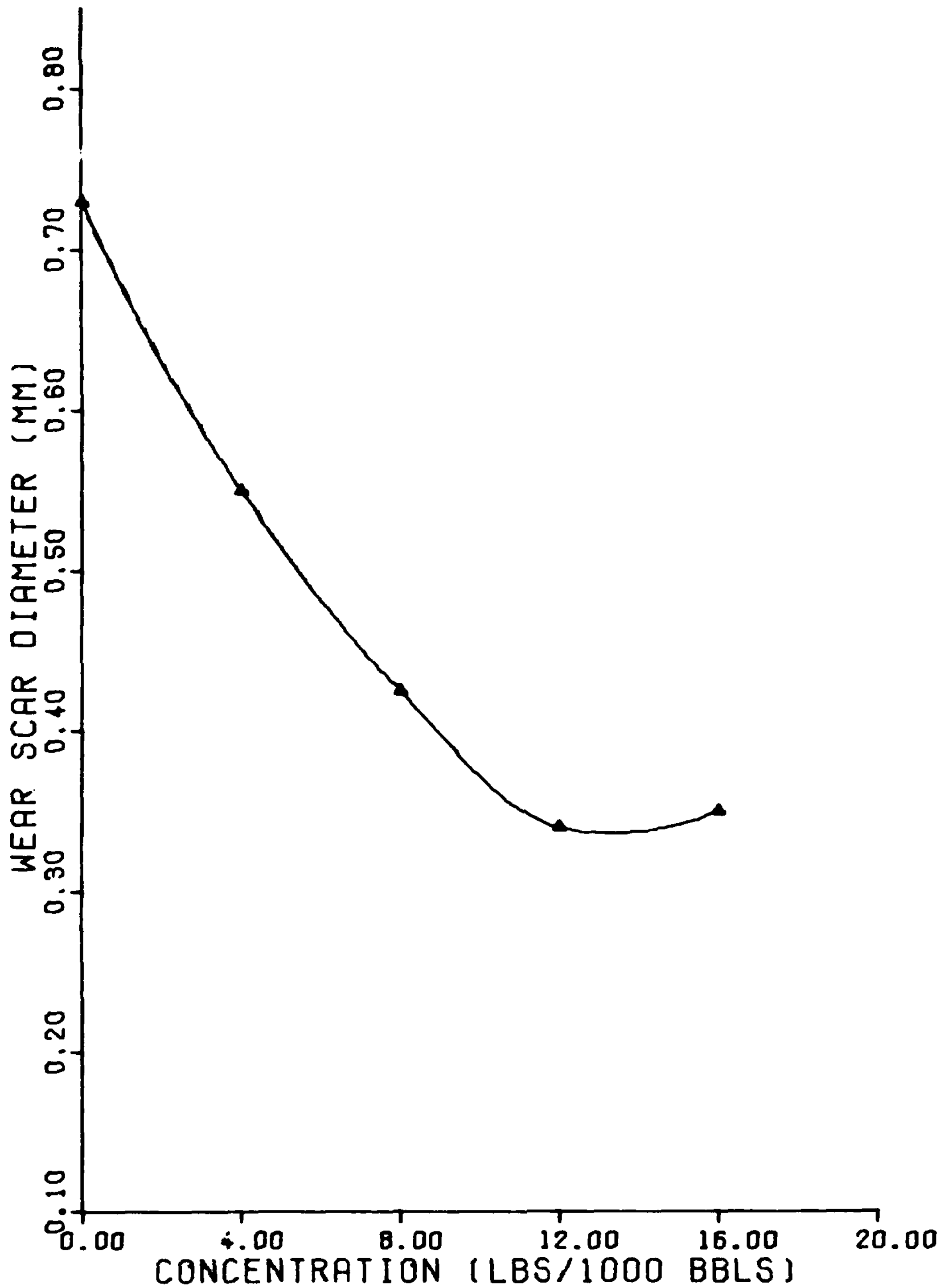

Figure 5. Wear Scar Diameter vs. Concentration of HITEC E-515 in Shell Sol 71

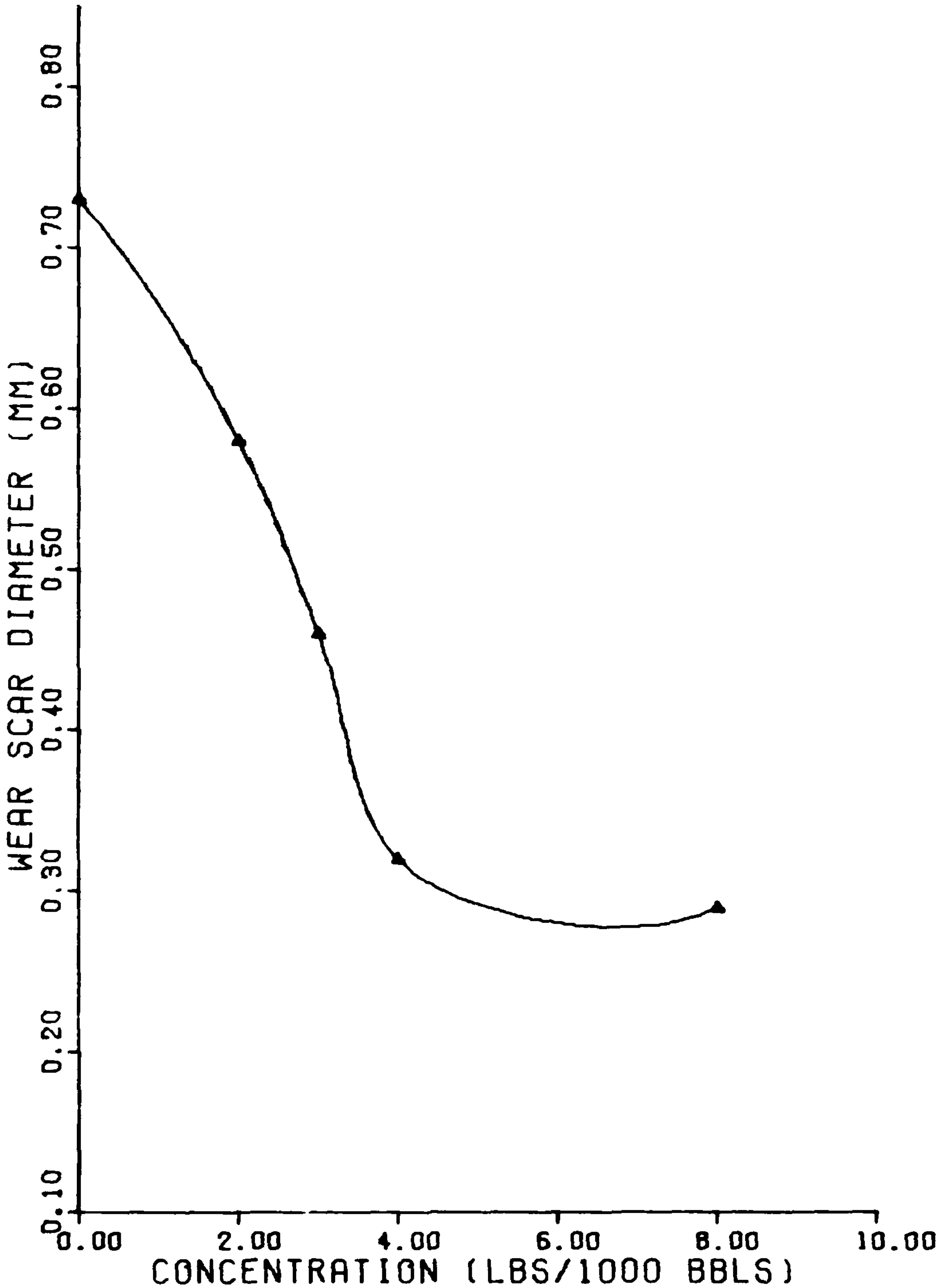

Figure 6. Wear Scar Diameter vs. Concentration of DCI-4A in Shell Sol 71

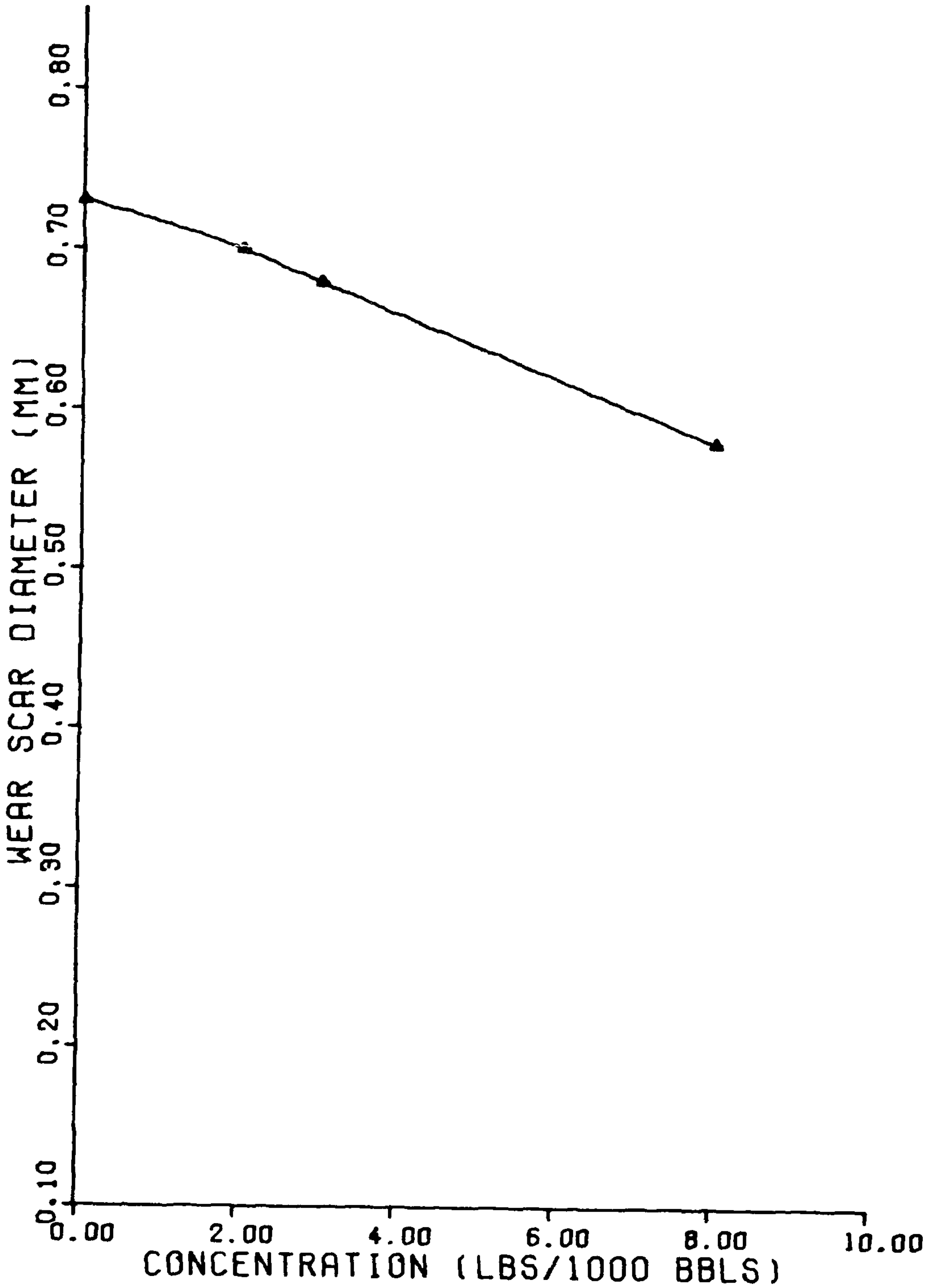

Figure 7. Wear Scar Diameter vs. Concentration of NALCO 5400-A in Shell Sol 71

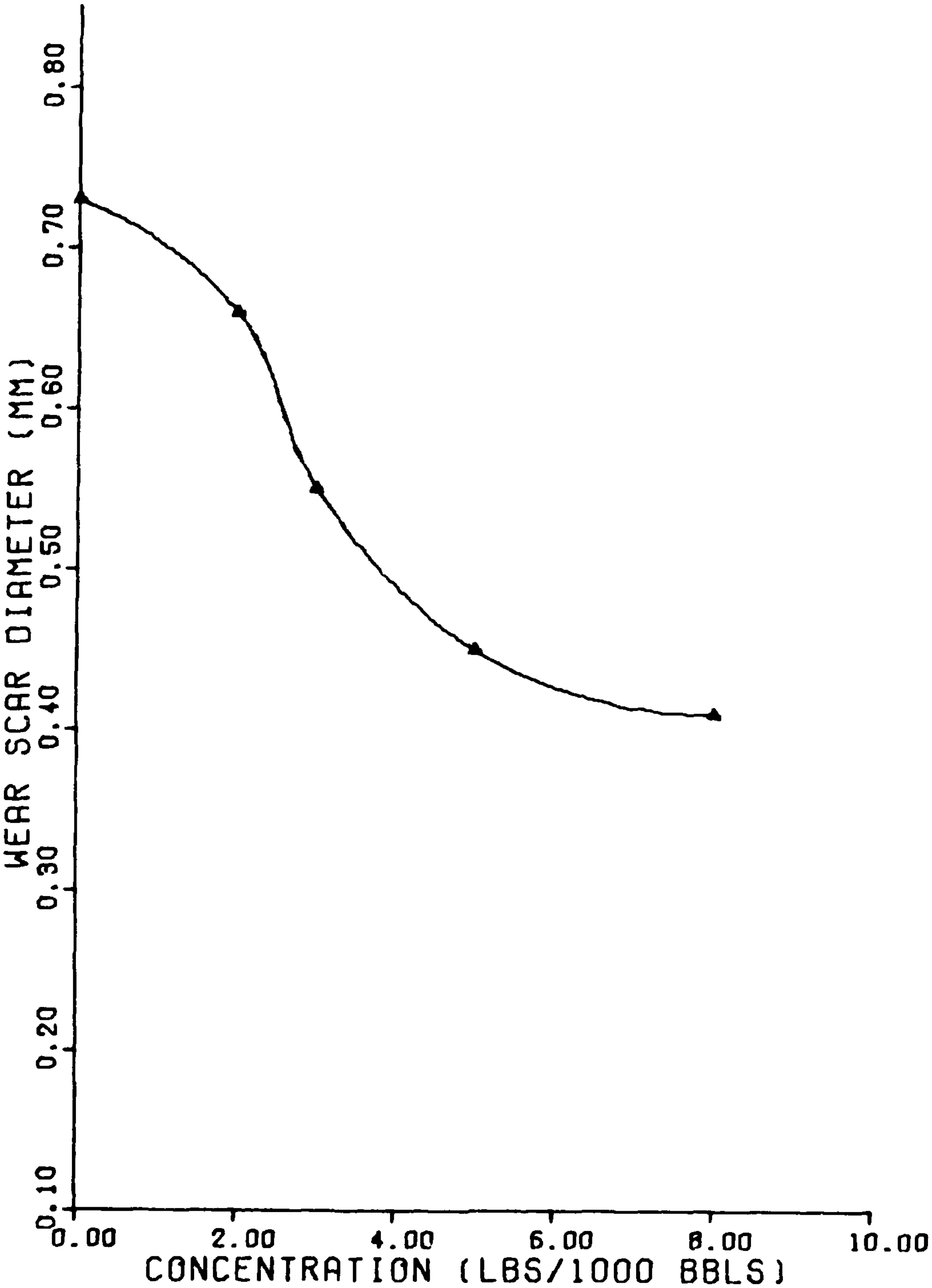

Figure 8. Wear Scar Diameter vs. Concentration of UNICOR-J in Shell Sol 71

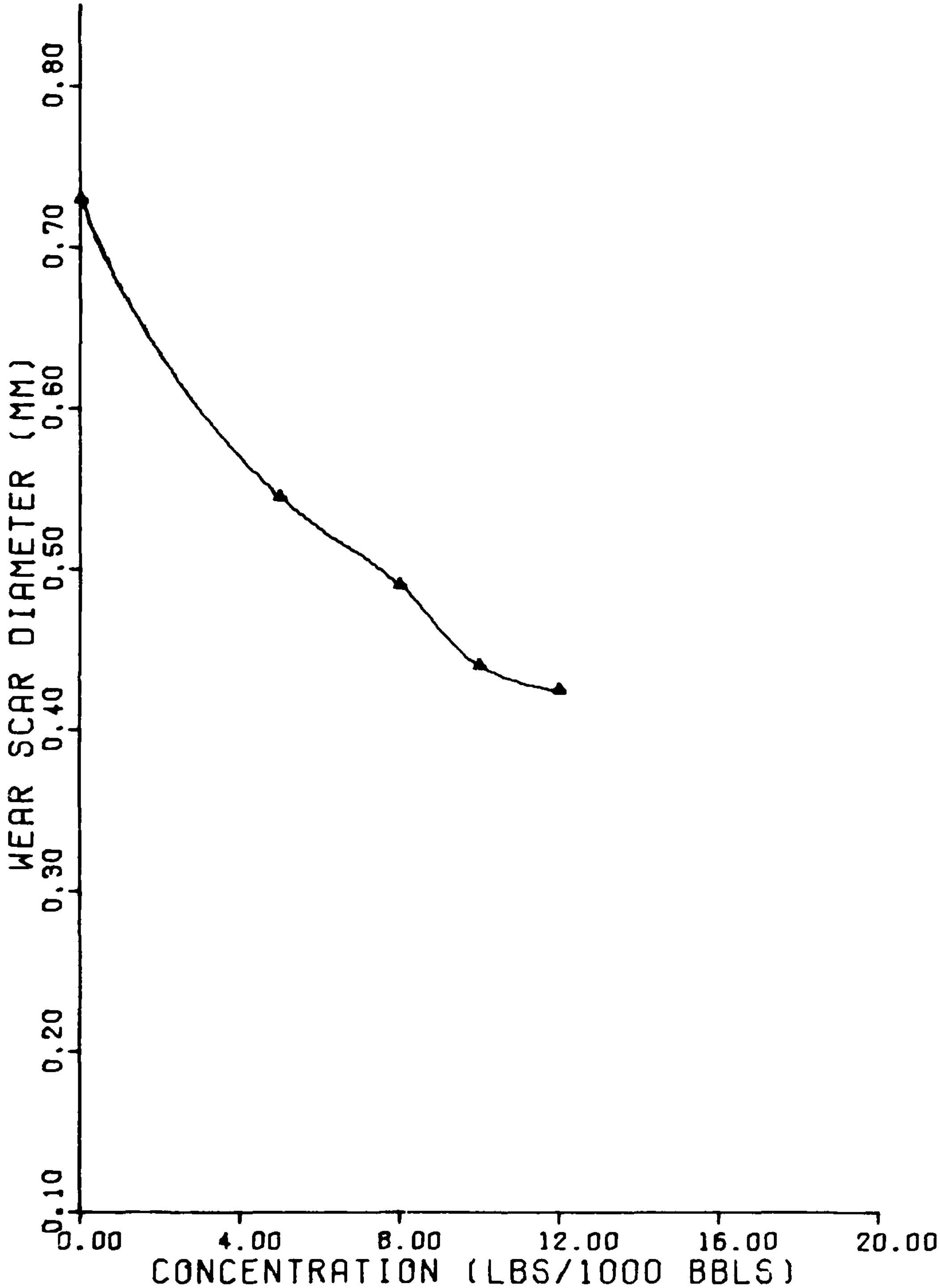

Figure 9. Wear Scar Diameter vs. Concentration of TOLAD 245 in Shell Sol 71

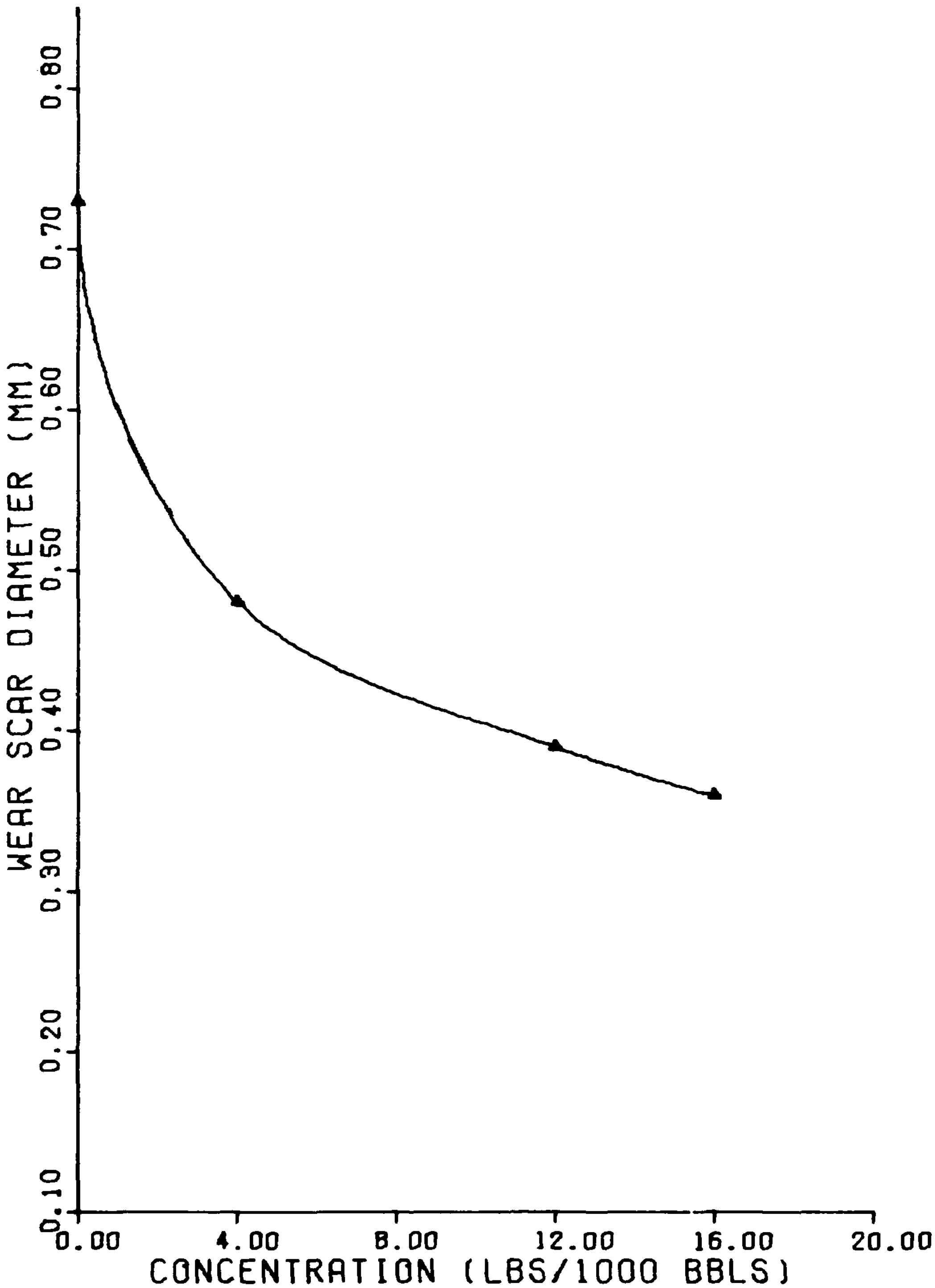

Figure 10. Wear Scar Diameter vs. Concentration of CONOCO T-60 in Shell Sol 71

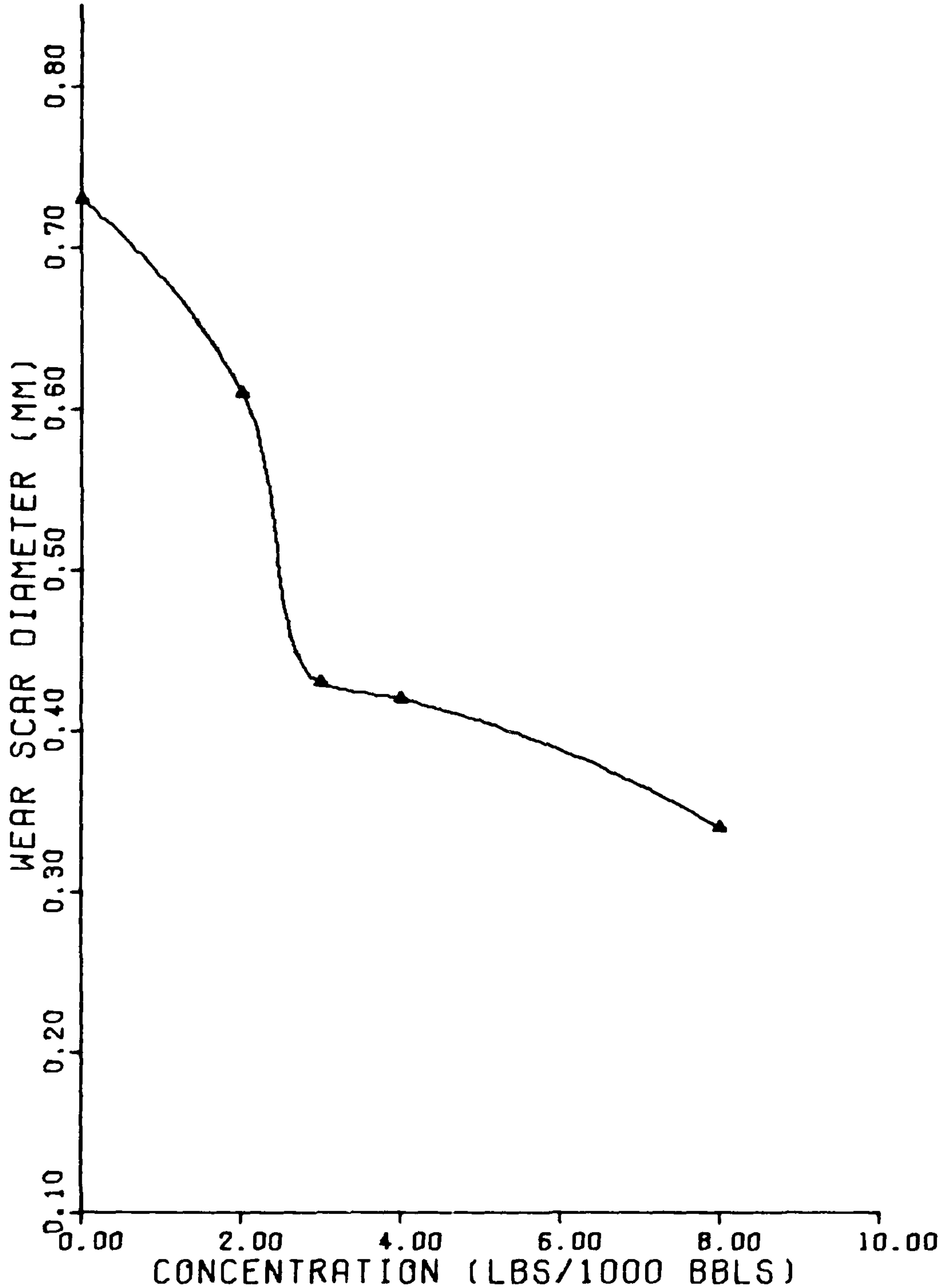

Figure 11. Wear Scar Diameter vs. Concentration of NALCO 5402 in Shell Sol 71

The effectiveness of the corrosion inhibitors was examined at their relative effective, minimum effective, and maximum allowable concentrations. Table III lists the change in wear scar diameter between the base fluid and the fluid with the additive at each of the three concentrations previously mentioned. For the relative effective concentration the change in WSD varied from .01 to .25. The ranking of additives, from least effective to most effective are: AFA-1, NALCO 5400-A, UNICOR-J, LUBRIZOL 541, TOLAD 244, PRI-19, NALCO 5402, DCI-4A, TOLAD 245, HITEC E-515, and CONOCO T-60.

At the minimum effective concentration, the change in WSD varied from .01 to .30. The order of effectiveness for the corrosion inhibitors at their minimum effective concentration is as follows: AFA-1, NALCO 5400-A, LUBRIZOL 541, TOLAD 244, UNICOR-J, PRI-19, TOLAD 245, DCI-4A, CONOCO T-60, HITEC E-515, and NALCO 5402.

The third concentration examined was the maximum allowable for each inhibitor. The change in WSD varied from .00 to .44. The order of effectiveness is as follows: AFA-1, NALCO 5400-A, TOLAD 244, LUBRIZOL 541, PRI-19, TOLAD 245, UNICOR-J, CONOCO T-60, HITEC E-515, NALCO 5402, and DCI-4A.

The application of the Spearman Rank Statistic to the relative/minimum concentration and minimum/maximum concentration relationships gave rank coefficients of .830 and .925 respectively. These coefficients indicate a correlation exists in each case at a level of significance of less than 1% and .1% respectively. In other words, the ranking of inhibitors by their WSD at any one of the three specified

TABLE III

EFFECT OF CORROSION INHIBITOR

CONCENTRATION ON WSD FOR SHELL SOL 71

DECREASE IN WEAR SCAR DIAMETER

ADDITIVE	RELATIVE EFFECTIVE CONCENTRATION	MINIMUM EFFECTIVE CONCENTRATION	MAXIMUM ALLOWABLE CONCENTRATION
AFA-1	.01	.0.	.00
LUBRIZOL 541	.10	.12	.21
TOLAD 244	.10	.16	.17
PRI-19	.11	.20	.29
HITEC E-515	.22	.29	.38
DCI-4A	.15	.27	.44
NALCO 5400-A	.03	.05	.14
UNICOR-J	.07	.18	.32
TOLAD 245	.19	.23	.30
CONOCO T-60	.25	.27	.37
NALCO 5402	.11	.30	.39

concentrations is applicable to the remaining two concentrations.

The corrosion inhibitors are normally added to JP-4 fuel by the refineries at their minimum effective concentrations. However as previously stated, the corrosion test does not determine the effectiveness of each inhibitor at the relative effective, minimum effective, or maximum allowable concentrations even though the test does establish these concentrations. Therefore, the minimum effective concentration for the inhibitors could be marginal in terms of lubricity.

The % effectiveness of the corrosion inhibitors can be evaluated with the Ball-on-Cylinder. In order to accomplish this, a concentration must be specified as the basis for the comparison. Ideally, the basis should be a concentration where the additives are 100% effective (lowest WSD possible). Since corrosion inhibitors are limited in the fuel by their maximum allowable concentration, the maximum allowable concentration is a more realistic basis for comparison and is the concentration at which the effectiveness of each inhibitor is considered to be 100%. The percent effectiveness of the inhibitors at their maximum effective concentration and at a concentration of two times their relative effective concentration are listed in Table IV. Four inhibitors (LUBRIZOL 541, DCI-4A, NALCO 5400-A, and UNICOR-J) are less than 70% effective at their minimum effective concentration. The inhibitor AFA-1 had an undefined per cent effectiveness since the change in WSD at its maximum allowable concentration was 0.00.

There does not appear to be any pattern to the shape of concentration curves for the additives. Some curves broke sharply with

increasing concentration, others moderately, and one gradually. However, this does suggest that there is a concentration higher than the minimum effective at which fewer than four inhibitors are under 70% effective.

The percent effectiveness of each inhibitor was also examined at 2 times its relative effective concentration by the use of its concentration curve. This is the highest concentration at which the effectiveness of all of the inhibitors can be compared statistically since it is also the maximum allowable concentration of TOLAD 244. The per cent effectiveness for the additives at this concentration are listed in Table IV. Only one additive, NALCO 5400-A, is under 70% effective.

TABLE IV

PER CENT EFFECTIVENESS OF LUBRICITY ADDITIVES AT THEIR RELATIVE EFFECTIVE AND TWO TIMES THEIR RELATIVE EFFECTIVE CONCENTRATIONS

	% Effectiveness	
Additive	Min. Effect. Conc.*	2 X Relative Eff Conc.
AFA-1	- * *	- * *
LUBRIZOL 541	57.1	71.4
TOLAD 244	94.1	100.0
PRI-19	100.0	100.0
HITEC E-515	76.3	94.7
DCI-4A	61.4	93.2
NALCO 5400-A	35.7	50.0
UNICOR-J	56.3	75.0
TOLAD 245	76.7	96.7
CONOCO T-60	73.0	81.1
NALCO 5402	76.9	100.0

* Min. Effect. Conc. = 1 1/2 X Rel. Eff. Conc.

* * Undefined since Δmaximum allowable WSD is 0.00

SECTION IV

EVALUATION OF LUBRICITY ADDITIVES AT 150°F

The fuel control and engine fuel pump have been the primary pieces of hardware affected by poor lubricity fuel. The fuel temperature entering the fuel control and fuel pump will vary due to the fuel system design and flight conditions of the aircraft. Each type of aircraft will have its own characteristic fuel system which affects the fuel temperature. For example, the fuel may be used to cool any of the following items: lubrication oil, hydraulic fluid, life support system, electronics, and the airframe. In older aircraft, the major amount of heat is added to the fuel in the oil heat exchanger which is located either up or down stream of the fuel control.

Because of the varying inlet temperature of the fuel to the fuel control and fuel pump, the question arose: what happens to the effectiveness of lubricity agents at higher than ambient fuel temperatures? An elevated fuel temperature test program was conducted with the Ball-on-Cylinder device in an effort to answer this question.

Two modifications were made to the Ball-on-Cylinder device for the test series. An exit drain was added to the test cell and a pressurized stainless steel container was used as a fuel feed reservoir. The system was set up so that at all times there would be a minimum of 50 ml of fuel in the test cell.

During the initial test series, it was found that 150°F was the maximum operating temperature for the Ball-on-Cylinder rig at a

compressed air flow rate of .2 ft ^{3}/min. At higher temperatures, the fuel vapors would condense on a beam and drip back into the test cell. In order to eliminate any contamination by the condensate, 150°F was the temperature used for this test series.

Eleven corrosion inhibitors at their maximum allowable concentration in Shell Sol 71 were tested on the modified Ball-on-Cylinder at the following operating conditions: 1000 gm load, 240 rpm speed, 2 cu ft/min dry air flow rate, and 1.2 ml/min fuel flow rate. The results are listed in Table V.

In the analysis of the results, the effectiveness of the corrosion inhibitors as lubricity agents at 75°F (see Section II) was used as the basis for comparison. The possible treatment effect caused by the temperature difference of the samples was evaluated using the Wilcoxon Signed Rank Test. A treatment effect was not found to exist at the 5.4% level of significance. Further analysis by applying the Spearman Rank Statistic gave a rank coefficient of .373. At the 5.4% level of significance, this implies the results at 150°F do not correlate with those at 75°F.

The results of this statistical analysis indicate that there is a definite change in the effectiveness of the lubricity agents at the higher temperature but without any change to the mean of the data. The additives which improved in their effectiveness at 150°F were AFA-1, LUBRIZOL 541, and TOLAD 244. One additive, CONOCO T-60, was unaffected by the higher temperature. The additives which degraded in their effectiveness at 150°F were PRI-19, HITEC E-515,

TABLE V

EFFECTIVENESS OF LUBRICITY ADDITIVES IN SHELL SOL 71 at 150°F

Additive	Wear Scar Diameter
None	.71
AFA-1	.36
LUBRIZOL 541	.42
TOLAD 244	.50
PRI-19	.46
HITEC E-515	.38
DCI-4A	.37
NALCO 5400-A	.65
UNICOR-J	.46
TOLAD 245	.51
CONOCO T-60	.36
NALCO 5402	.39

DCI-4A, NALCO 5400-A, UNICOR-J, TOLAD 245, and NALCO 5402. However, the most drastic relative change in effectiveness was obtained with AFA-1. It went from the least effective additive at 75°F to the most effective at 150°F. For older aircraft which have the oil heat exchanger upstream of the fuel control and modern aircraft which utilize the fuel as a major heat sink, the AFA-1 additive appears to be the superior fuel lubricity agent.

The drastic change in the relative effectiveness of AFA-1 can be explained by its comparison to extreme pressure lubricants. Extreme pressure lubricants are normally hydrocarbons which contain active radicals such as phosphorus, chlorine, or sulphur. The mechanism for these additives is dependent on the temperature of the environment. The temperature must be high enough to cause the additive to decompose. After thermal decomposition has occurred, the product reacts with the metal surface to form a compound which reduces friction and wear of the metal. At temperatures below the thermal decomposition temperature of the additive, the additive probably will not be effective.[8] As shown in Appendix B, the additive AFA-1 contains 5-5.5% phosphorus. At the base fluid temperature of 75°F, the additive was ineffective. However at the base fluid temperature of 150°F, the additive become active and very effective.

As shown in Appendix B, two other additives also contain phosphorus. They are HITEC E-515 and NALCO 5400-A with .30-40% and 4.75-5.75% phosphorus respectively. Unlike AFA-1, these two decreased in their effectiveness at the higher base fluid temperature. However, the possibility exists that these additives may become more effective at a base fluid temperature higher than 150°F.

SECTION V

CONCLUSION

1. The 11 corrosion inhibitors on QPL-25017-9 are effective as lubricity agents in either JP-5 or JP-4.

2. Shell Sol 71 is a suitable base fluid for the lubricity evaluation of the corrosion inhibitors. Shell Sol 71 is superior to JP-4 and JP-5 for evaluating the effects of additives at very low concentrations.

3. The effectiveness of the corrosion inhibitors can be detected at concentrations less than their relative effective concentration in Shell Sol 71.

4. The effectiveness of the corrosion inhibitors varies at the three concentrations tested: the relative effective, the minimum effective, and the maximum allowable.

5. The rank effectiveness of the inhibitors in Shell Sol 71 at their relative effectiveness, minimum effective, and maximum allowable concentrations did correlate. Any of the three concentrations may be used to evaluate the additives on a ranking basis.

6. The corrosion inhibitors are currently required in the fuel at a concentration of 1 1/2 times the relative effective concentration (minimum allowable). At their minimum allowable concentrations, four of the inhibitors are less than 70% as effective as at their maximum allowable concentration.

7. At a concentration of 2 times the relative effective concentration, only one inhibitor was less than 70% as effective as at its maximum allowable concentration. If lubricity problems are encountered in aircraft which use JP-4 fuel, one solution may be to raise

the minimum allowable concentration to 2 times the relative effective value. Another solution would be to remove the less effective corrosion inhibitor from the QPL.

8. The temperature of 150°F is the maximum temperature at which the Furey Ball-on-Cylinder can be operated in its present setup. However if a controlled environment box was used, a higher operational temperature could be achieved.

9. The effectiveness of the corrosion inhibitors in Shell Sol 71 at 75°F did not correlate with the effectiveness at 150°F.

10. The AFA-1 at 75°F in Shell Sol 71 is the least effective additive. However, at 150°F, it became the most effective. It is believed that this additive is operating like an extreme pressure lubricant. These results indicate AFA-1 would be the superior lubricity agent in aircraft which utilize the fuel as a high heat sink.

11. There are two corrosion inhibitors, HITEC E-515 and NALCO 5400-A, which may also function like extreme pressure lubricants. However at 150°F, no improvement in lubricity was found. The possibility does exist that the temperature of the base fluid was not high enough to activate the phosphorus compounds present in the additives.

12. Although the relative lubricity of fuels can be examined with the Ball-on-Cylinder, the relationship between WSD and fuel lubricity has not been firmly established. Before this device could be made into a specification test method, additonal data would be needed to correlate this device with either field problems or hardware problems (pump or fuel control test). Also, a similar hardware correlation program is needed to confirm that the relative ranking of the effectiveness of the corrosion inhibitors with the Ball-on-Cylinder is correct.

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APPENDIX A

SPEARMAN RANK CORRELATION STATISTIC

In data analysis, the correlations between different test rigs on the same test specimens are often sought. This is a paired replicate data system with N pairs of observations (X_1, Y_1), (X_2, Y_2). . . ., (X_N, Y_n).

One method of correlation analysis applicable to paired replicate data is the Spearman Rank Statistic. This statistic is non-parametric. The only assumptions made about the X and Y populations are that they are continuous. In other words, they may be other than normal.[9]

The statistic's hypothesises are centered on the calculated rank coefficient, r. The null hypothesis for two-sided test is as follows:

H_o: $r = 0$ X and Y are independent

The alternate hypothesis is:

H_1: $r \neq 0$ X and Y are dependent

The procedure for the application of the statistic to the data is straightforward. The X_i values are arranged in order of size and a rank from low to high is assigned to each. The same is done to the Y_i values. In either case if a tie occurs, the average rank is used. Next the difference between the paired X_i rank and Y_i rank is denoted as D_i. The rank correlation coefficient, r, is calculated from the following equation:

$$r = 1 - 6 \sum_{i=1}^{N} {}^2 / (N(N^2 - 1))$$

The value of r may range from 1 (perfect agreement) to -1 (opposite agreement). The null hypothesis is rejected if $r \geq K(\alpha_1, N)$ or $r \leq -k(\alpha_2, N)$ where r is the rank coefficient and the constants, $K(\alpha_1, N)$ and $k(\alpha_2, N)$ satisfy either $P_o(r \geq -k(\alpha_1, N) = \alpha_1$, which is the probability that $r \geq -k(\alpha_2, N)$, or $P_o(r \leq -k(\alpha_2, N) = \alpha_2$ which is the probability that $r \leq -K(\alpha_2, N)$. The level of significance, α, of the test is equal to $\alpha_1 + \alpha_2$ which is the probability of rejecting H_o when it is true.

If the value of r is known, the level of significance, α, at which the null hypothesis is just accepted may be approximated by the use of tabulated statistical tables of N, α, and $K(\frac{\alpha}{2}, N)$. This is accomplished by setting $k(\frac{\alpha}{2}, N)$ equal to r. Since N and $K(\frac{\alpha}{2}, N)$ are known, the value of α may be found directly in the table.

An example of the application of the Spearman Rank Statistic to the JP-4/Shell Sol 71 data from Section II is described below. The data, ranks, D_i, and D_i^2 are included in Table A.1. Since there are 13 fuels, the value of N is 13. The rank coefficient is calculated as follows:

$$r = 1 - 6 \sum_{i=1}^{N=11} D_i^{\ 2} / 11(11^2 - 1)$$

$$r = 1 - 6\ (38.0) / 1320 = 1 - .127$$

$$r - .873$$

TABLE A.1

APPLICATION OF SPEARMAN RANK CORRELATION STATISTIC

ADDITIVE	WSD FOR JP-4 BASE FLUID (mm)	X_i RANK	WSD FOR SHELL SOL 71 BASE (mm)	Y_i RANK	D_i	D_i^2
AFA-1	.53	11.0	.73	11.0	0.0	0.0
LUBRIZOL 541	.42	8.0	.52	8.0	0.0	0.0
TOLAD 244	.45	9.0	.56	9.0	0.0	0.0
PRI-19	.39	7.0	.44	7.0	0.0	0.0
HITEC E-515	.34	2.5	.35	3.0	.5	.25
DCI-4A	.34	2.5	.29	1.0	-1.5	2.25
NALCO 5400-A	.50	10.0	.59	10.0	0.0	0.0
UNICOR-J	.38	5.5	.41	5.0	- .5	.25
TOLAD 245	.37	4.0	.43	6.0	2.0	4.0
CONOCO T-60	.31	1.0	.36	4.0	3.0	9.0
NALCO 5402	.38	5.5	.34	2.0	-3.5	12.25

The null hypothesis, H_o: $r = 0$, is rejected if $r \geq k(\alpha_1, 13)$. For a 5% level of significance, the value of -k(.25, 11) is .602 which was obtained from Table A - 30a of Reference 9. Therefore, the JP-4/Shell Sol 71 results correlate at the 5% level of significance. The lowest level of significance at which the null hypothesis is rejected may also be approximated from this table. The largest value of $k(\alpha, N)$ shown in the tables for N = 1 is .847 with α = .001. Since the calculated rank coefficient, .873, is still greater than k (.0005, 11), .847, the hypothesis is rejected at a level of significance less than .1%.

QUALIFICATION VALIDATED	
OCTOBER	1972

QPL-25017-9
3 November 1972
SUPERSEDING
QPL-25017-8
30 April 1971

APPENDIX B

QPL-25017-9

QUALIFIED PRODUCTS LIST
OF
PRODUCTS QUALIFIED UNDER MILITARY SPECIFICATION
MIL-I-25017

FSC 6850

INHIBITOR, CORROSION, FUEL SOLUBLE

This list has been prepared for use by or for the Government in the procurement of products covered by the subject specification and such listing of a product is not intended to and does not connote indorsement of the product by the Department of Defense. All products listed herein have been qualified under the requirements for the product as specified in the latest effective issue of the applicable specification. This list is subject to change without notice; revision or amendment of this list will be issued as necessary. The listing of a product does not release the supplier from compliance with the specification requirements.

The activity responsible for this Qualified Products List is the Air Force Aero Propulsion Laboratory (SFF).

GOVERNMENT DESIGNATION		MANUFACTURER'S DESIGNATION	TEST OR QUALIFICATION REFERENCE	MANUFACTURER'S NAME AND ADDRESS
Table I, additives approved for use in fuels meeting VV-G-001690, VV-G-76, MIL-C-3056, MIL-G-5572 and MIL-T-5624.				
Relative effective conc lbs/1000 bbls	3	AFA-1	SFF Letter of approval 5 Mar 71	E.I. Dupont De Nemours & Co. Chambers Works Deepwater, N.J. 08023
Minimum effective conc lbs/1000 bbls	4.5			
Maximum allowable conc lbs/1000 bbls	12			
Specific gravity 60/60°F	0.91-0.93			
Viscosity, centistokes at 100°F	85-105			
Flash point, °F minimum	134			
Neutralization number	124-136			
Ash content, % maximum	0.04			
Pour point, °F maximum	0			
Phosphorus, %	5.00-5.50			

GOVERNMENT DESIGNATION		MANUFACTURER'S DESIGNATION	TEST OR QUALIFICATION REFERENCE	MANUFACTURER'S NAME AND ADDRESS
Relative effective conc lbs/1000 bbls	2	LUBRIZOL 541	SFF Letter of Approval 5 Mar 71	Lubrizol Corp. P.O. Box 428 Painsville OH 44077
Minimum effective conc lbs/1000 bbls	3			
Maximum allowable conc lbs/1000 bbls	6			
Specific gravity 60/60°F	0.95-0.97			
Viscosity, centistokes at 100°F	34-48			
Flash point, °F minimum	57			
Neutralization number	152-172			
Ash content, % maximum	0.04			
Pour point, °F maximum	0			
Phosphorus, %	0			
Relative effective conc lbs/1000 bbls	3	TOLAD 244	SFF Letter of Approval 5 Mar 71	Tretolite Division 369 Marshall Ave. St. Louis MO 63119 and Tretolite Division 200 S. Puente St. Brea CA 63119
Minimum effective conc lbs/1000 bbls	4.5			
Maximum allowable conc lbs/1000 bbls	6			
Specific gravity, 60/60°F	0.90-0.92			
Viscosity, centistokes at 100°F	45-68			
Flash point, °F minimum	105			
Neutralization number	80-92			
Ash content, % maximum	0.04			
Pour point, °F maximum	0			
Phosphorus, %	0			

Table II, additives approved for use in fuels meeting VV-G-001690, VV-G-76, MIL-G-3056, and MIL-T-5624.

Relative effective conc lbs/1000 bbls	2	PRI-19	SSF Letter of Approval 5 Mar 71	Apollo Chemical Co. 250 Delawanna Ave. Clifton NJ 070[illegible] and Apollo Chemical Co. 338 Wilson Ave. Newark NJ 07105
Minimum effective conc lbs/1000 bbls	3			
Maximum allowable conc lbs/1000 bbls	8			
Specific gravity 60/60°	0.89-0.91			

GOVERNMENT DESIGNATION		MANUFACTURER'S DESIGNATION	TEST OR QUALIFICATION REFERENCE	MANUFACTURER'S NAME AND ADDRESS
Viscosity, centistokes at 100°F	60-85			
Flash point, °F	119			
Neutralization number	90-98			
Ash content, % maximum	0.04			
Pour point, °F maximum	0			
Phosphorus, %	0			
Relative effective conc lbs/1000 bbls	5	HITEC E-515	SFF Letter of Approval 5 Mar 71	Monsanto Chemical Co. Nitro, W. Va. 25143
Minimum effective conc lbs/1000 bbls	7.5			
Maximum allowable conc lbs/1000 bbls	16			
Specific gravity 60/60°F	0.86-0.88			
Viscosity, centistokes at 100°F	45-63			
Flash point, °F minimum	140			
Neutralization number	93-101			
Ash content, % maximum	0.04			
Pour point, °F maximum	0			
Phosphorus, %	0.30-0.40			
Relative effective conc lbs/1000 bbls	3	HITEC E-534		
Minimum effective conc lbs/1000 bbls	4.5			
Maximum allowable conc lbs/1000 bbls	8			
Specific gravity, 60/60°F	0.88-0.90			
Viscosity, centistokes at 100°F	50-70			
Flash point, °F minimum	150			
Neutralization number	94-112			
Ash content, % maximum	0.04			
Pour point, °F maximum	0			
Phosphorus, %	0.62-0.78			

GOVERNMENT DESIGNATION		MANUFACTURER'S DESIGNATION	TEST OR QUALIFICATION REFERENCE	MANUFACTURER'S NAME AND ADDRESS
Relative effective conc lbs/1000 bbls	2	DCI-4A	SFF Letter of Approval 2 Oct 72	E.I. DuPont De Nemours & Co. Chambers Works Deepwater NJ 08023
Minimum effective conc lbs/1000 bbls	3			
Maximum allowable conc lbs/1000 bbls	8			
Specific gravity 60/60°F	0.93-0.95			
Viscosity, centistokes at 100°F	48-68			
Flash point, °F	80			
Neutralization number	97-117			
Ash content, % maximum	0.04			
Pour point, °F maximum	0			
Phosphorus, %	0			
Relative effective conc lbs/1000 bbls	2	NALCO 5400-A	SFF Letter of Approval 11 Apr 72	Nalco Chemical Co. Sugar Land TX 77478
Minimum effective conc lbs/1000 bbls	3			
Maximum allowable conc lbs/1000 bbls	8			
Specific gravity 60/60°F	0.91-0.94			
Viscosity, centistokes at 100°F	102-138			
Flash point, °F minimum	100			
Neutralization number	125-150			
Ash content, % maximum	0.04			
Pour point, °F maximum	0			
Phosphorus, %	4.75-5.75			
Relative effective conc lbs/1000 bbls	2	UNICOR-J	SFF Letter of Approval 22 Mar 72	UOP Process Div. 8400 Joliet Rd. McCook IL 60525
Minimum effective conc lbs/1000 bbls	3			
Maximum allowable conc lbs/1000 bbls	8			
Specific gravity 60/60°F	0.93-0.94			
Viscosity, centistokes at 100°F	70-80			

GOVERNMENT DESIGNATION		MANUFACTURER'S DESIGNATION	TEST OR QUALIFICATION REFERENCE	MANUFACTURER'S NAME AND ADDRESS
Flash point, °F minimum	125			
Neutralization number	110-126			
Ash content, % maximum	0.04			
Pour point, °F maximum	0			
Phosphorus, %	0			
Relative effective conc lbs/1000 bbls	5	TOLAD 245	SFF Letter of Approval 5 Mar 71	Tretolite Division 396 Marshall Ave. St. Louis MO 63119
Minimum effective conc lbs/1000 bbls	7.5			
Maximum allowable conc lbs/1000 bbls	12			
Specific gravity, 60/60°F	0.94-0.96			
Viscosity, centistokes at 100°F	7-14			
Flash point, °F minimum	90			
Neutralization number	50-62			
Ash content, % maximum	0.04			
Pour point, °F maximum	0			
Phosphorus, %	0			

TABLE III, additives approved for use in fuel meeting MIL-T-5624

Relative effective conc lbs/1000 bbls	4	CONOCO T-60	SFF Letter of Approval 5 Mar 71	McNutt Industries 6800 S. Council Oklahoma City OK 73101
Minimum effective conc lbs/1000 bbls	6			
Maximum allowable conc lbs/1000 bbls	16			
Specific gravity 60/60°F	0.85-0.88			
Viscosity, centistokes at 100°F	45-57			
Flash point, °F minimum	100			
Neutralization number	95-105			
Ash content, % maximum	0.04			
Pour point, °F maximum	0			
Phosphorus, %	0			

GOVERNMENT DESIGNATION		MANUFACTURER'S DESIGNATION	TEST OR QUALIFICATION REFERENCE	MANUFACTURER'S NAME AND ADDRESS
Relative effective conc lbs/100 bbls	2	NALCO 5402	SFF Letter of Approval 18 Aug 72	Nalco Chemical Co. Sugar Land TX 77478
Minimum effective conc lbs/1000 bbls	3			
Maximum allowable conc lbs/1000 bbls	8			
Specific gravity 60/60°F	0.93-0.96			
Viscosity, centistokes at 100°F	160-210			
Flash point, °F minimum	100			
Neutralization number	108-132			
Ash content, % maximum	0.04			
Pour point, °F maximum	0			
Phosphorus, %	0			

APPENDIX C

WILCOXON SIGNED RANK STATISTIC

In certain data analysis situations, the statistical interest is on whether the median of a population has shifted. An example is the evaluation of treatment effects on a population. The Wilcoxon Signed Rank Test is a non-parametric statistic used for this purpose on paired replicate observations such as (X_1, Y_1), (X_2, Y_2), $\cdots$, (X_N, Y_N) where N is the number of observation pairs.

In the statistic, Z_i is equal to $Y_i - X_i$. The model is

$Z_i = \theta + e_i$ where $i = 1, 2, \cdots, N$.

The e_i's are unobservable random variables and θ is the unknown treatment effect. The e_i's are assumed to be mutually indpendent and come from a continuous population. Therefore, the sum of the e's is equal to zero. The null hypothesis for the model is as follows:

H_o: $\theta = 0$

The alternative hypothesis for a two sided test is:

H_i: $\theta \neq 0$

The procedure for this statistic consists of four main steps which are as follows:[10]

1. Let Ψ_i equal 1 if $Z_i > 0$ or 0 if $Z_i < 0$.
2. Let R_i denote the rank of the ordered (Z_i). In the case of tied data, the average rank is used. If $Z_i = 0$ then the data point is discarded and N is decreased by 1.
3. Let T^+ denote the sum of all positive sign ranks which is expressed symbolically as follows:

$$T^{+} = \sum_{i=1}^{N} R_i \, W_i$$

4. Reject H_0 (two sided test) if $T^{+} \geq t(\alpha_2, n)$ or $T^{+} \leq \frac{N(N+1)}{2} - t(\alpha_1, n)$. The lower level of significance, α_1, is equal to the probability that $T^{+} \geq \frac{N(N+1)}{2} - t(\alpha_2, n)$. The level of significance, α, is equal to $\alpha_1 + \alpha_2$.

An example of the application of the Wilcoxon Signed Rank Test to the JP-4/Shell Sol 71 data in Section II is described below. The data, Z_i, α_i, R_i, and T^{+} is tabulated in Table C.1. The value of T^{+} is 58. The null hypothesis is rejected if $T^{+} \geq t(\alpha_2, N)$ or $T^{+} \leq \frac{N(N+1)}{2} - t(\alpha_1, N)$. For $\alpha_1 = \alpha_2, = .027$ and $N = 11$, $t(.027, 11)$ is equal to 55. Since T^{+} is greater than 53, the null hypothesis is rejected at the .054 level of significance. A treatment effect does exist at the .054 level of significance.

TABLE C.1.

APPLICATION OF WILCOXON SIGNED RANK STATISTIC

Additive	W S D for JP-4 Base Fluid (mm)	W S D for Shell Sol 71 Base Fluid (mm)	Z_i	Ψ_i	R_i	T^+
AFA-1	.53	.73	.20	1	11.0	11.0
LUBRIZOL 541	.42	.52	.10	1	9.0	9.0
TOLAD 244	.45	.56	.11	1	10.0	10.0
PRI-19	.39	.44	.05	1	5.0	5.0
HITEC E-515	.34	.35	.01	1	1.0	1.0
DCI-4A	.34	.29	-.05	0	5.0	0.0
NALCO 5400-A	.50	.59	.09	1	8.0	8.0
UNICOR-J	.38	.41	.03	1	2.0	2.0
TOLAD 245	.37	.43	.06	1	7.0	7.0
CONOCO T-60	.31	.36	.05	1	5.0	5.0
NALCO 5402	.38	.34	-.04	0	3.0	0.0